

# Chemistry

## Lecture 6

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### Carboxylic Acids and Macromolecules

#### Outline:

- ✚ Nomenclature
- ✚ Classification
- ✚ Physical properties
- ✚ Preparations of Carboxylic acids
- ✚ Reactivity
- ❖ Proteins
- ❖ Enzymes

#### Carboxylic Acids (C.A's):

##### Nomenclature

#### Common Names of Carboxylic Acids:

- ◆ Common names of carboxylic acids are to be remembered.

Chemical formula	Common name	Chemical formula	Common name
HCOOH	Formic acid	(COOH) <sub>2</sub>	Oxalic acid
CH <sub>3</sub> COOH	Acetic acid	HOOC-CH <sub>2</sub> -COOH	Malonic acid
CH <sub>3</sub> CH <sub>2</sub> COOH	Propionic acid	HOOC-(CH <sub>2</sub> ) <sub>2</sub> -COOH	Succinic acid
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	Butyric acid	HOOC-(CH <sub>2</sub> ) <sub>3</sub> -COOH	Glutaric acid
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH	Valeric acid	HOOC-(CH <sub>2</sub> ) <sub>6</sub> -COOH	Adipic acid
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOH	Caproic acid	$\begin{array}{c} \text{HC}-\text{COOH} \\ \parallel \\ \text{HC}-\text{COOH} \end{array}$	Maleic acid
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOH	Palmitic acid		Cis-form
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH	Stearic acid	$\begin{array}{c} \text{HOOC}-\text{CH} \\ \parallel \\ \text{CH}-\text{COOH} \end{array}$	Fumaric acid
C <sub>17</sub> H <sub>33</sub> COOH	Oleic acid		Trans-form

#### IUPAC Rules for Carboxylic Acids:

##### Selection of Chain:

- ⚙ Select the longest continuous carbon chain containing carboxyl group (-COOH).
- ⚙ If more than one chain is of same length, then select one with maximum no. of carboxyl groups.
- ⚙ If no. carboxyl groups is same, select one with maximum substituents and if substituents are also same, then select any.

### Numbering:

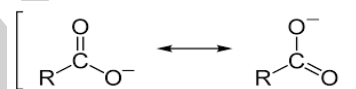
- Start numbering from the end of carboxyl group.

### Naming:

- Name alkane is replaced with "alkanoic acid".  
Position of substituent-name of substituent alkanoic acid
- If more than one carboxyl groups are present then use dioic acid, trioic acid etc.

### Classification

- Alkanoic acid
- General formula is  $C_nH_{2n+1}COOH$  or  $C_nH_{2n}O_2$
- Carboxyl (carbonyl + hydroxyl) group ( $-COOH$ ) is the functional group
- Both carbon and oxygen of carbonyl group are  $sp^2$  hybridized (planar triangular)
- While oxygen in form of  $-OH$  is  $sp^3$  hybridized
- Can show resonance between two highly E.N O-atoms making it stable than carbonyl compounds.



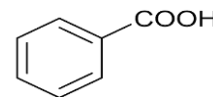
### Types:

- On basis of number of  $-COOH$  groups:

Mono C.A's (fatty acids)	Di C.A's	Tri C.A's
Possess one $-COOH$	Possess two $-COOH$	Possess three $-COOH$
Methanoic ( $HCOOH$ )	Oxalic acid ( $(COOH)_2$ )	Citric acid
Ethanoic acid ( $CH_3COOH$ )	Tartaric acid $HOOC-CH(OH)-CH(OH)-COOH$	$HOOC-CH_2-C(OH)(COOH)-CH_2-COOH$

- On basis of aromaticity (nature of R group):

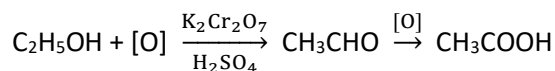
- Aliphatic C.A's:** Having no benzene ring
- Aromatic C.A's:** Possess at least one benzene ring like benzoic acid



### Preparation of Carboxylic Acids

#### 1. From primary Alcohols and Aldehydes:

- Direct oxidation in presence of oxidizing agents.
- Primary alcohols oxidize to aldehydes which in same conditions give carboxylic acids
- No. of carbon atoms remain same throughout
- Aldehydes can directly be oxidized to respective carboxylic acids



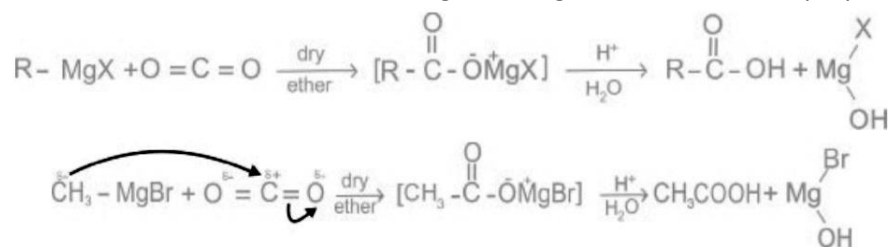
#### 2. From Alkane nitriles:

- Acid hydrolysis of alkane nitriles produces carboxylic acid
- $-CN$  group converts  $-COOH$  group

- Discussed in lecture of aldehyde & ketones

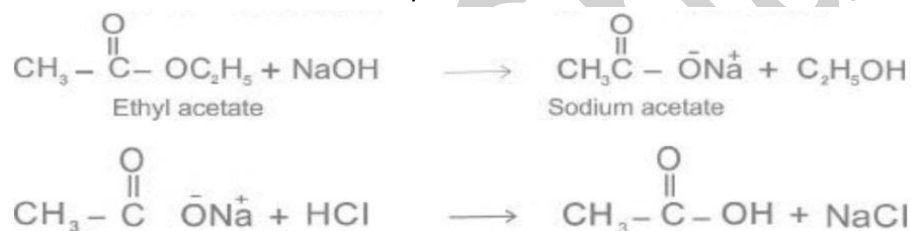
### 3. From Grignard's Reagent:

- Grignard reagent on reaction with  $\text{CO}_2$  produces C.A
- One carbon is extra in C.A than Grignard reagent from which it is prepared



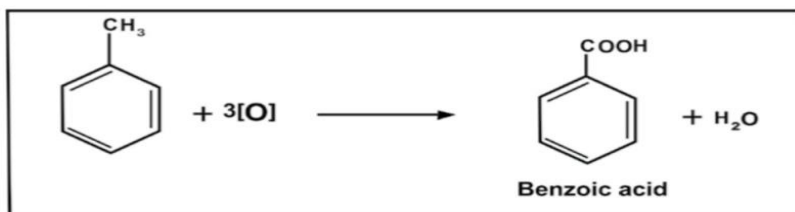
### 4. By the Hydrolysis of Esters:

- Esters on boiling with conc. NaOH give salt of C.A
- The salt when treated with dil. HCl yields C.A

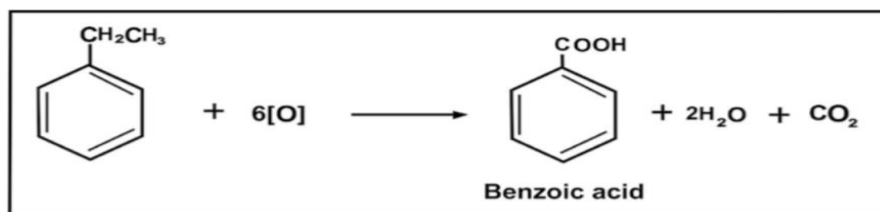


### 5. By the oxidation of alkyl benzene:

- Strong oxidizing agent ( $\text{KMnO}_4/\text{H}_2\text{SO}_4$ ) is used
- Pink colour of  $\text{KMnO}_4$  discharges



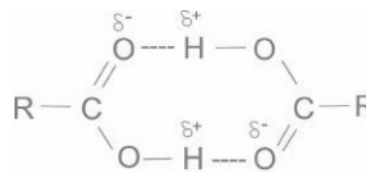
Whatever the length of an alkyl group may be it gives only one carboxyl group. Moreover the colour of  $\text{KMnO}_4$  is discharged. Therefore this reaction is used as a test for alkylbenzenes.



### Physical Properties

- ◆ C1-C3 are colorless liquids with pungent smell
- ◆ C4-C6 are colorless liquids with unpleasant smell

- ◆ First four members are very soluble in water due to H-bonding
- ◆ Solubility in water decreases with increasing molecular mass (C-chain)
- ◆ Two molecules of carboxylic acids form H-bonding with each other in non-aqueous solvent like benzene
- ◆ Exist as dimer form (8 atoms in ring)  
Therefore showing double molecular mass in non-polar solvent.
- ◆ Boiling points are higher due to H-bonding and increases with C-chain increase  
HCOOH (100°C)[373 K], CH<sub>3</sub>COOH (118°C)[391 K], CH<sub>3</sub>CH<sub>2</sub>COOH (141°C)[424 K]
- ◆ Melting points increase irregularly with increase in C-chain
- ◆ Melting points C.A's with even no. of C-atoms are higher than the next lower and higher members containing odd no. of C-atoms because in case of even no. of C-atoms -COOH and -CH<sub>3</sub> are opposite to each other making it symmetrical molecule.  
CH<sub>3</sub>CH<sub>2</sub>COOH (-22°C)[251 K], CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH (-6°C)[267 K],  
CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOH (-36°C)[237 K]



## Reactions of Carboxylic Acids

**Reactivity/acidity of carboxylic acids decreases with increase in carbon chain length.**

### (A) Reactions Involving H-atom of Carboxyl Group:

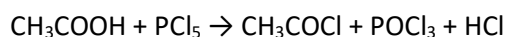
- ◆ O-H bond breaks
- ◆ H is replaced
- ◆ Salt formation (Acid base reaction)
  - + C.A's produce salt + water with Bases (like NaOH)  
CH<sub>3</sub>COOH + NaOH → CH<sub>3</sub>COONa + H<sub>2</sub>O
  - + C.A's produce salt + water + CO<sub>2</sub> with Carbonates (like Na<sub>2</sub>CO<sub>3</sub>) and Bicarbonates (like NaHCO<sub>3</sub>)  
2CH<sub>3</sub>COOH + Na<sub>2</sub>CO<sub>3</sub> → 2CH<sub>3</sub>COONa + H<sub>2</sub>O + CO<sub>2</sub>
  - + C.A's produce salt + H<sub>2</sub> gas with Metals (like Na)  
2CH<sub>3</sub>COOH + 2Na → 2CH<sub>3</sub>COONa + H<sub>2</sub>

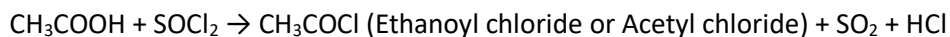
### (B) Reactions Involving -OH Group of Carboxyl Group:

- ◆ C-O bond breaks
- ◆ -OH group is replaced
- ◆ Derivatives are prepared
- ◆ All derivatives on hydrolysis yield same carboxylic acid from which they were formed
- ◆ Nucleophilic substitution reactions (mostly)

#### 1. With PCl<sub>5</sub>, SOCl<sub>2</sub>:

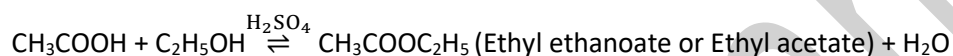
- Nucleophile is Cl<sup>-</sup>
- Products are called Acid chlorides (Common) or Alkanoyl chlorides (IUPAC)
- Most reactive derivative of C.A's, reduces to primary alcohols





## 2. Ester Formation:

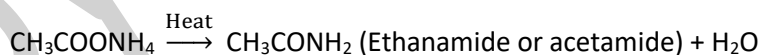
- Nucleophile is lone pair of oxygen on  $\text{C}_2\text{H}_5\ddot{\text{O}}\text{H}$  or  $\ddot{\text{O}}\text{C}_2\text{H}_5$
- Products are called alkyl alkanoate (IUPAC)
- Esters have fruity smell
- $\text{H}_2\text{SO}_4$  is used as catalyst and dehydrating agent
- Protonates the C.A
- Only derivative of C.A whose formation is result of a reversible reaction
- Also termed as condensation reaction



Ester	Flavour
Amyl acetate	Banana
Isobutyl formate	Raspberry
Benzyl acetate	Jasmine
Ethyl butyrate	Pineapple
Amyl butyrate	Apricot
Octyl acetate	Orange

## 3. Amide Formation:

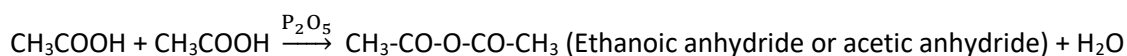
- Reaction with ammonia
- Nucleophile is lone pair of Nitrogen
- Products are called Acid amides (Common) or Alkanamide (IUPAC)
- Last reactive derivative of C.A's
- Only derivative which is formed in two steps
- First step is the formation of ammonium acetate (stable salt)
- Second step is the formation of Alkanamide as result of dehydration of ammonium acetate on heating



- ✚ Ethanamide on base hydrolysis gives sodium/potassium salt of carboxylic acid
- ✚ Ethanamide on dehydration with  $\text{P}_2\text{O}_5$  gives ethane nitrile

## 4. Formation of Acid Anhydride:

- Dehydration with  $\text{P}_2\text{O}_5$
- It is also a condensation reaction
- Products are called Acid anhydride (Common) or Alkanoic anhydride (IUPAC)



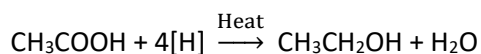
### Reactivity order of derivatives:

Acylchloride > Anhydride > Ester > Amide

### (C) Reactions Involving Carboxyl Group: Reduction reactions

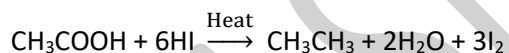
#### 1. Partial Reduction:

- In presence of  $\text{LiAlH}_4$
- Products are alcohols with same number of C-atoms



#### 2. Complete Reduction:

- In presence of  $\text{HI/P}$
- Products are alkanes with same number of C-atoms



**Uses of Acetic acid:** Colorless liquid which freezes like ice in pure state at  $17^\circ\text{C}$  called glacial acetic acid.

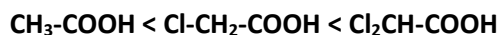
- ✿ As coagulant for latex in rubber industry
- ✿ In manufacture of plastic
- ✿ Synthetic fibre
- ✿ As local irritant
- ✿ As solvent in laboratory
- ✿ In manufacture of pickle
- ✿ Seasoning of food

### Acidity of Carboxylic Acids

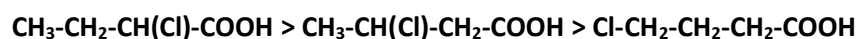
Carboxylic acids > Phenol > Water > Alcohols > Ethyne > Ethene

- Formic acid is the strongest among all C.A's
- Acidic strength decreases with increase in C-chain length

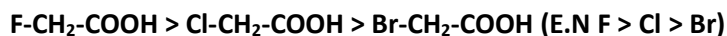
### Acidic Strength of Chloro Substituted C.A's:



- ◆ Cl is an electron withdrawing group making acid strong by increasing the polarity of O-H bond
- ◆ Position of Cl also affects the acidic strength
- ◆ Cl closer to carboxylic group will have more withdrawing effect.



- ◆ Some example of withdrawing groups (-CN, -NO<sub>2</sub>, F, Br etc)



- ◆ Higher the value of K<sub>a</sub>, stronger is the acid or vice versa
- ◆ Higher the value of P<sub>Ka</sub>, weaker is the acid or vice versa

## Macromolecules

- ☞ Large molecules made up of small molecules and are classified as;
  - ❖ **Inorganic** : Giant molecules i.e. diamond, graphite
  - ❖ **Organic**:
    - **Biopolymers (natural)**: Lipids, Proteins, Nucleic acid, Carbohydrates
    - **Synthetic Polymers (manmade)**

### Polymer:

- Derived from Greek letters i.e. “poly” mean many and “mer” means parts
- Basic unit is monomer

### Degree of Polymerization (DP):

- No. of repeating units in a polymer
- Used to calculate the molecular mass of polymer

$$\text{Molecular mass of polymer} = \text{Molecular mass of repeating unit (can be monomer)} \times \text{DP}$$

$$\text{Molecular formula times greater than empirical formula} = \text{Molar mass of Polymer} / \text{Molar mass of repeating unit}$$

## Proteins

The extremely complicated high molecular weight organic materials which upon complete hydrolysis yield amino acids are called proteins”.

- ❖ Derived from Greek letter “Proteois” meaning of “Prime importance”
- ❖ Building of animal body
- ❖ Human body contains at least 10,000 different kinds of proteins
- ❖ Elements in all proteins are C, H, O, N and may have P
- ❖ Trace elements are Fe, Cu, I, Mn, S, Zn
- ❖ Amino acids are building blocks of proteins
- ❖ Basis for the major structural components of animal and human tissue
- ❖ Involved in processes such as food digestion, cell structure, catalysis, movement etc
- ❖ Most of the proteins possess three structure i.e. primary, secondary and tertiary
- ❖ Some proteins also possess a fourth structure called quaternary

## Classification of Proteins:

### (a) Based on the physico-chemical properties:

**(1) Simple proteins** These proteins on hydrolysis yield only amino acids or their derivatives

**Examples:** (i) **Globulins** are insoluble in water but soluble in dilute salt solutions. They are found in animals i.e. lactoglobulin is found in muscles and in plants

(ii) **Legumin and collagen** are present in connective tissues. Most abundant proteins in animal kingdom forming 25-35% of body protein

(iii) **Albumin** principal component of egg white and soluble in water, dilute salt solutions

**(2) Compound or conjugated proteins** These proteins are attached to non-protein groups, these non-protein parts are prosthetic groups

**Examples:** Phospho-proteins, Lipoproteins, Nucleoproteins, Mucoprotein, Glycoprotein

**(3) Derived proteins** These proteins are derived from simple and conjugated proteins by heat, physical forces or chemical forces

**Examples:** Proteases enzymes, Peptones, Oligopeptides, Polypeptides, Proteans

### (b) Based on their functions:

(i) Regulatory or Hormonal proteins

(ii) Structural proteins

(iii) Transport protein

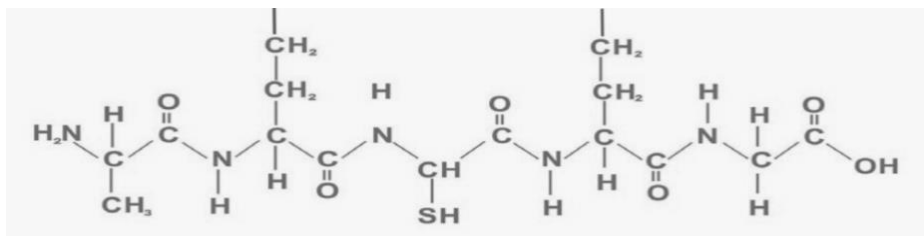
(iv) Genetic proteins

## Structure of Proteins

### Primary Structure:

◆ Referred as by;

- ✚ Number of amino acids in polypeptide chain
- ✚ Nature of amino acids in polypeptide chain
- ✚ Sequence of amino acids in polypeptide chain



◆ Simple peptide (amide) linkage present



- ◆ Hydrolysis yields different products

Proteins  $\Rightarrow$  Proteoses  $\Rightarrow$  Peptones  $\Rightarrow$  Polypeptides  $\Rightarrow$   $\alpha$ -amino acids

No. of Peptide bonds in polypeptide = no. of amino acids in polypeptide chain – 1

### Secondary Structure:

- ◆ Regular coiling of polypeptide chains due to **H-bonding** between  $\diagup\text{C=O}$  and  $\diagdown\text{NH}$  of nearby amino acids
- ◆ Two conformations possible
  - $\alpha$ -Helix (spiral):**
    - Can be clockwise or anti clockwise
    - Peptide chains i.e.  $\diagup\text{C=O}$  and  $\diagdown\text{NH}$  are vertically adjacent to each other
    - On average there are 27 amino acid units for each turn of helix
  - $\beta$ -Structure or Pleated Sheet Structure:**
    - Peptide chain line up side by side
    - $\diagup\text{C=O}$  and  $\diagdown\text{NH}$  in plane of sheet
    - **Parallel** (peptide chains run in same direction)
    - **Anti-parallel** (peptide chains run in different direction)

### Tertiary Structure:

- ◆ The three dimensional twisting and folding of the polypeptide chain results in the tertiary structure of proteins

### Quaternary Structure:

- ◆ Quaternary means four. This is the fourth phase in creation of a protein.
- ◆ The arrangement of multiple folded protein or coiling protein molecules in a multi-subunit complex.
- ◆ Hydrogen bonding, salt bridges and disulfide bonds hold various chains into a particular geometry.

### Importance of Proteins:

- Take essential part in formation of protoplasm which is the essence of all forms of life
- Nucleoproteins (complex protein with nucleic acids) serves as heredity carrier (transfer of Genes)
- Enzymes as biological catalysts are proteins
- Hemoglobin in transport of oxygen in blood. As hormones which have regulatory functions (insulin, thyroxine)

**Industrially**  $\rightarrow$  i. Leather made by tanning of hides. This is essentially a precipitation of the proteins with tannic acid

ii. Gelatin obtained by heating bones, skin and tendons in water. Used in bakery goods

iii. Casein used in manufacture of buttons and buckles

iv. Proteins obtained from the soya bean are used for the manufacture of plastics

## Enzymes

Enzymes can be defined as the reaction catalysts of biological systems produced by living cells and are capable of catalyzing chemical reactions.

- Highly specific in action
- May speed up reactions by a factor of upto  $10^{20}$
- Most enzymatic reactions are reversible
- The enzymes which are from same organisms, catalyze the same reaction but are chemically and physically distinct from each other are called **Isoenzymes**
- Follow lock and key model where enzyme acts as an active site where substrate molecule binds to convert into product
- It can be either pure protein or having some non-protein component along with protein
- The protein component of the enzyme is called **apoenzyme** and the non-protein component is called the **co-factor or co-enzyme** (inorganic ions and complex organic or metallo-organic molecules).

**Examples:** Inorganic co-factors  $\Rightarrow$   $\text{Fe}^{2+}$ (chrome oxidase)  $\text{Zn}^{2+}$ (carbonic anhydrase) and  $\text{Mg}^{2+}$ (-glucose 6- phosphatase)

Vitamins as  $\Rightarrow$  Nicotinamide adenine dinucleotide contains nicotinamide vitamin and thiamine pyrophosphatase contains vitamin B1.

- ☞ While naming the enzymes, suffix-“ase” is added to the name of the substrate on which the enzyme acts, for example, urease, sucrase, cellulase are the enzymes, which act upon the substrates urea, sucrose and cellulose respectively.

## Classification of Enzymes

IUB classified enzymes into six main types.

### 1. Oxidoreductases:

- Catalyze oxidation-reduction reaction (transfer of electron)
- Oxidase, dehydrogenase, peroxidase

### 2. Transferases:

- Catalyze exchange of functional group such as phosphate or acyl between two compounds
- Phospho-transferases

### 3. Hydrolases:

- Catalyze hydrolysis
- Include proteases called protolytic enzymes

### 4. Lyases:

- Catalyze the addition of ammonia, water or  $\text{CO}_2$  to double bonds or removal of these to from double bond
- Phospho-glyceromutases

### 5. Isomerases:

- Catalyze the transfer of groups within the molecules to yield isomeric forms of the substrate
- Conversion of fumaric acid to maleic acid in presence of fumarase enzyme

### 6. Ligases:

- Link two molecules together through the breaking of high energy bonds
- Acetyl-S-COH, a carboxylase and Succinic thiokinase

## Factors affecting Enzyme Activity

### (i) Substrate & enzyme concentration:

Rate  $\propto$  concentration of substrate

Rate  $\propto \sqrt{\text{concentration of enzyme}}$

**(ii) Temperature:**

- Enzyme gives maximum activity at temperature called optimum temperature i.e. 37°C for animal enzyme and 60°C for some plant enzyme
- Rate of enzymatic reaction increases with increase in temperature (upto a limit b'coz high temp. destroys enzyme) and decreases with decrease in temperature

**(iii) pH:**

- Enzyme gives maximum activity at pH called optimum pH i.e. 6.4 to 6.9 for salivary amylase (digestion), pepsin (working in stomach) active in acidic pH = 2 and trypsin (working in small intestine) active in alkaline pH = 8-9

**(iv) Other substances:**

- Activator or co-enzyme increases the activity of enzyme
- Inhibitor decreases the activity of enzyme

**(v) Radiation:**

Enzyme becomes inactive when exposed to UV light, beta rays, gamma rays and X-rays

**Importance of Enzymes**

- ❖ **Alkaline phosphatase** is raised in rickets and obstructive jaundice
- ❖ **Lactic dehydrogenase or LDH-1** is raised in heart disease
- ❖ **Thrombin** is used locally to stop bleeding
- ❖ **L-asparaginase** in treatment of blood cancer in children